FePt magnetic nanoparticles: *a SANS study of agglomeration effects*

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Nanoparticles offer exciting possibilities to study fundamental physics and create new technologies in catalysis, sensors, biology and medicine, and data storage. In particular self-assembled FePt magnetic nanoparticles offer the potential to store data at areal densities > 1 Tbit/in^2. This potential arises from the high anisotropy ($L1_0$) phase of approximately equi-atomic FePt, that allows particles of ~20 Å diameter to be thermally stable at room temperature. However, in order to create the $L1_0$ phase of FePt it is necessary to anneal at temperatures in excess of 500 °C, typically for times of 30 minutes [1]. This gives rise to a number of thermally activated processes including the desired phase transformation, oxidation and particle agglomeration. In this study we use small-angle neutron scattering (SANS) to obtain information on agglomeration as a function of annealing conditions and show that for all the conditions significant clustering occurs. Complementary magnetisation measurements demonstrate that a significant fraction of the particles are superparamagnetic indicating the complete $L1_0$ ordering is not achieved. However coercivities of up to 13 kOe at room temperature were readily obtained, demonstrating that self-assembled nanoparticles do indeed offer significant potential as recording media.

FePt nanoparticles were prepared using a solution chemistry approach and deposited onto double-sided Si substrates using the polymer mediated, layer-by-layer technique described previously [2]. This resulted in films consisting of 3 layers of 40 Å $Fe_{58}Pt_{42}$ self-assembled particles, as shown for similar films in figure 1. The polymer-mediated approach results in nanoparticles with an extremely narrow size distribution, typically σ/mean < 5 %, and a well defined periodicity. The as-deposited films were annealed under a range of temperatures (580 to 800 °C) and times (2 to 120 minutes). Magnetisation measurements as a function of temperature were completed for all films. A subset of the annealed films were investigated using the D11 diffractometer with a neutron wavelength of λ = 4.5 Å. The neutrons were collimated to give a beam diameter of 16 mm. Data were collected at three detector positions in order to scan a q range of 0.012 – 0.3 Å-1. The small volume of material meant that it was necessary to stack a number of samples to increase signal to noise ratio. However, significant counting times were required to obtain statistically meaningful data.

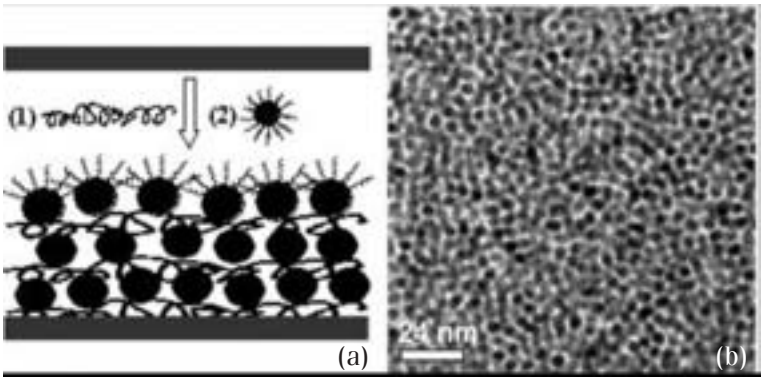

Figure 1: (a) Illustration of polymer-mediated self-assembly of nanoparticles, (1) is the polymer and (2) is the surfactant coated particle. (b) TEM bright field image of 60 Å $Fe_{50}Pt_{50}$ nanoparticles showing that as-deposited the particles have a very narrow size distribution, typically s/mean < 5 % for this process, and that the particles have a well defined separation [2].

Figure 2 shows diffraction images for an as-deposited sample. The coherent diffraction ring is immediately apparent, demonstrating the regularity of the as-deposited nanoparticle films as previously shown using electron microscopy [1]. Integrating round the detector gives an interparticle distance of 65 Å with a distribution σ = 12 Å. This diffraction ring was absent for all of the annealed samples over the q-range measured (q = 0.012 - 0.3 Å^{-1})

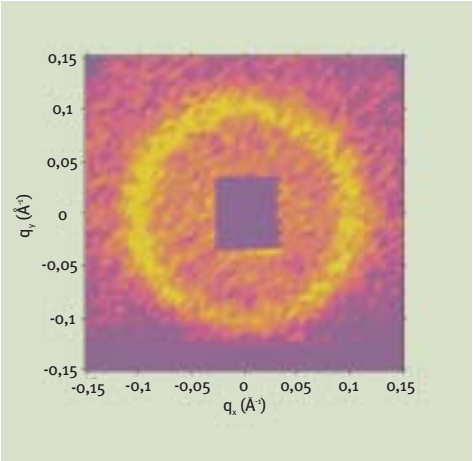

Figure 2: Diffraction image measured at room temperature for as-deposited $Fe_{58}Pt_{42}$ nanoparticles with a diameter of 40 Å and a separation of 65 Å.

indicating that annealing disrupted the inter-particle ordering. To estimate particle sizes from the SANS data it was necessary to compare the measured data with simulations. A number of models based on the hard sphere, Percus Yevick approximation were produced and compared to the experimental data. Given that the nanoparticle films are known to consist initially of 40 Å particles with a 65 Å centre-to-centre spacing, a polydisperse model of interacting particles with a Schultz-gamma distribution of sizes described by Griffith *et al.* [3] was adopted. However, the salient features of the data were reproduced for a number of different models giving confidence that the results obtained did not depend on the details of the model used.

Figure 3 shows SANS data, simulations of the data and the particle/cluster size implied by the simulation. The SANS data indicate that significant agglomeration occurs for all three samples. Using the median particle diameter to characterise the distribution, the particle/cluster size increases from 40 Å for the as-deposited film to 62 Å for the film annealed at 580 °C for 30 minutes and to 160 Å for the 650 °C / 5 minutes film. In the case of the 700 °C / 5 minutes film the median size appears to increase rather dramatically, giving a median cluster diameter of 660 Å. The details of this large increase in size for the 700 °C / 5 minutes film remain to be fully explained. Complementary magnetic measurements show that the temperature dependence of coercivity is significantly less for this sample which also suggests a large increase in volume as thermally activated magnetisation reversal will be less significant.

SANS data shows that a high degree of inter-particle ordering is achieved when $Fe_{58}Pt_{42}$ nanoparticles, with as-deposited diameters of 40 Å, are deposited onto Si substrates in an organic binder. Subsequent annealing at temperatures greater than 500 °C, necessary for the FePt to form the high magnetic anisotropy $L1_0$ phase, results in the particles forming clusters, the size of which increases with annealing temperature.

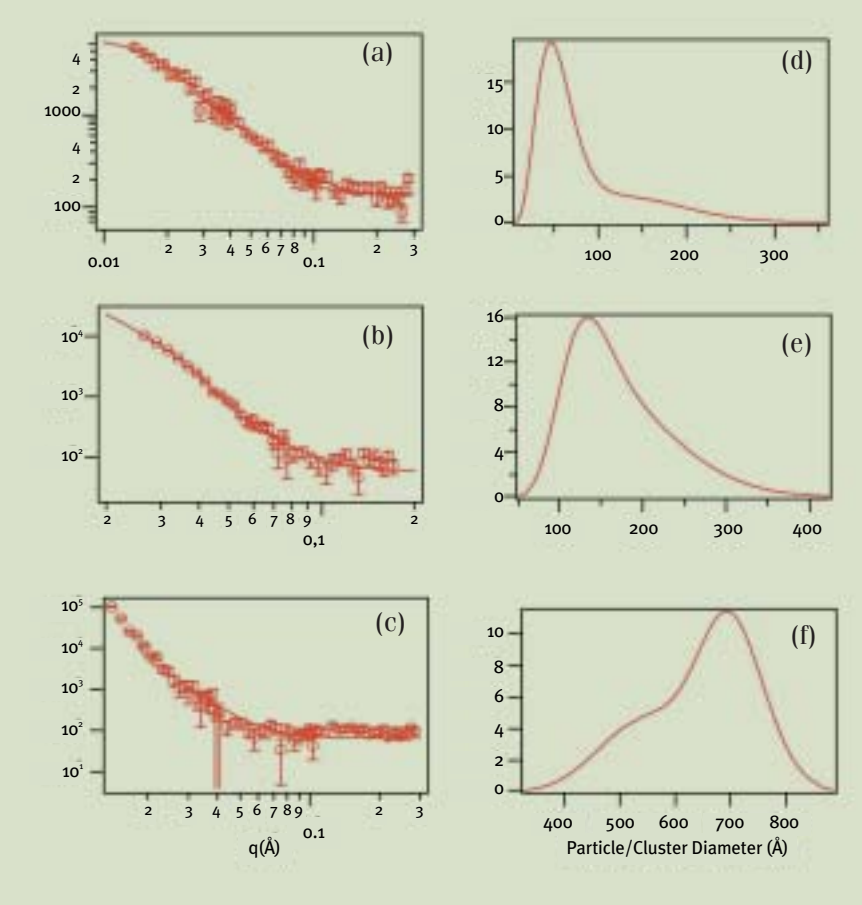

Figure 3: SANS data with simulation (solid line) for three FePt nanoparticle films annealed at (a) 580 °C / 30 minutes, (b) 650 °C / 5 minutes and (c) 700 °C / 5 minutes. All measurements were carried out at room temperature (d-f) particle size distributions obtained from simulation of the SANS data using the hard sphere, polydisperse interacting model of Griffith et al. [3].

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